AD-A228 118

pproved
o. 0704-0188

REPORT DOCUMENTATION

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Approved for Public Release Distribution Unlimited
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of North Carolina	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) Campus Box 3290 Chapel Hill, NC 27599-3290		7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N0014-89-J-1734

8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification) UNCLASSIFIED: Identification of a Novel Tetragonally-Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex (3-chloroanilinium)$_8$ [CuCl$_6$]Cl$_4$

12. PERSONAL AUTHOR(S) Denise A. Tucker, Peter S. White, Kathleen L. Trojan, Martin L. Kirk and William E. Hatfield

13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM_____ TO_____	14. DATE OF REPORT (Year, Month, Day) 1990 October 12	15. PAGE COUNT 41

16. SUPPLEMENTARY NOTATION
Technical Report No. 39

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) hexachlorocuprate(II) 3-chloroanilinium tetragonally compressed octahedron.
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A monomeric hexachlorocuprate(II) ion has been found in the compound (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, CuC$_{48}$H$_{56}$Cl$_{18}$N$_8$. The compound crystallizes in the triclinic space group P$\bar{1}$ with unit cell dimensions $\underline{a}$ = 8.5488(16) Å, $\underline{b}$ = 13.964(6) Å, $\underline{c}$ = 14.273(7) Å, α = 90.46(4)°, β = 107.82(3)°, and γ = 102.11(3)° with Z = 1. The coordination about the discrete [CuCl$_6$]$^{4-}$ ion is that of a tetragonally compressed octahedron with bond distances Cu-Cl(1) = 2.2773(11) Å, Cu-Cl(2) = 2.6061(18) Å, and Cu-Cl(3) = 2.6086(20) Å. The two short bond distances are on the order frequently seen for copper-chloride bonds, but the remaining four bond distances are remarkably long for in-plane 4 + 2 coordination. The Cl(1)-Cu-Cl(1a), Cl(2)-Cu-Cl(2a), and Cl(3)-Cu-Cl(3a) angles are strictly 180°, and the 12 remaining Cl(i)-Cu-Cl(j) angles

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL

DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. Abstract

differ from 90° by 0.4 to 1.0°. The EPR spectrum of a powdered sample is of the "reversed" nature indicative of a ^2A ground state with $g_∥ = 2.04$ and $g_⊥ = 2.20$. Magnetic susceptibility data provide evidence for antiferromagnetic interactions between the hexachlorocuprate cations, since there is a maximum in the magnetic susceptibility near 10 K. The data may be approximated by Heisenberg chain theory with $J = -5.6$ cm^{-1}, $g = 2.00$, and an interchain exchange parameter $J' = -2.1$ cm^{-1}.

18. Subject Terms

magnetic susceptibility

antiferromagnetic interactions

Heisenberg chain theory

A-1

Identification of a Novel Tetragonally-Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$

by

Denise A. Tucker, Peter S. White, Kathleen L. Trojan,

Martin L. Kirk and William E. Hatfield

The Department of Chemistry, The University of North
Carolina at Chapel Hill, North Carolina, 27599, U.S.A.

Prepared for Publication in

INORGANIC CHEMISTRY

Identification of a Novel Tetragonally-Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex, (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$

Denise A. Tucker, Peter S. White, Kathleen L. Trojan,[1] Martin L. Kirk, and William E. Hatfield[*]

Abstract

A monomeric hexachlorocuprate(II) ion has been found in the compound (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, CuC$_{48}$H$_{56}$Cl$_{18}$N$_8$. The compound crystallizes in the triclinic space group P$\bar{1}$ with unit cell dimensions $\underline{a}$ = 8.5488(16) Å, $\underline{b}$ = 13.964(6) Å, $\underline{c}$ = 14.273(7) Å, α = 90.46(4)°, β = 107.82(3)°, and γ = 102.11(3)° with Z = 1. The coordination about the discrete [CuCl$_6$]$^{4-}$ ion is that of a tetragonally compressed octahedron with bond distances Cu-Cl(1) = 2.2773(11) Å, Cu-Cl(2) = 2.6061(18) Å, and Cu-Cl(3) = 2.6086(20) Å. The two short bond distances are on the order frequently seen for copper-chloride bonds, but the remaining four bond distances are remarkably long for in-plane 4 + 2 coordination. The Cl(1)-

Cu-Cl(1a), Cl(2)-Cu-Cl(2a), and Cl(3)-Cu-Cl(3a) angles are strictly 180°, and the 12 remaining Cl(i)-Cu-Cl(j) angles differ from 90° by 0.4 to 1.0°. The EPR spectrum of a powdered sample is of the "reversed" nature indicative of a ^2A ground state with $g_{\parallel} = 2.06$ and $g_{\perp} = 2.19$. Magnetic susceptibility data provide evidence for antiferromagnetic interactions between the hexachlorocuprate cations, since there is a maximum in the magnetic susceptibility near 10 K. The data may be approximated by Heisenberg chain theory with $J = -5.6$ cm^{-1}, $g = 2.00$, and an interchain exchange parameter $J' = -2.1$ cm^{-1}.

Introduction

Substituted anilinium cations form an interesting and novel series of complexes with chlorocuprates. Many of these have very unusual properties. For example, the parent member of the series (anilinium)$_2$ tetrachlorocuprate(II) is ferromagnetic[2] as a result of orthogonal superexchange interactions in the extended planar array of bridged (CuCl$_4$) units. In the structure of (anilinium)$_2$ tetrachlorocuprate(II),[3] there are four short copper-chloride bond distances of 2.3 Å and two long copper-chloride bond distances of 2.9 Å, with two of the short bonds being normal to the rectangular lattice. The anilinium ions are perpendicular to the chlorocuprate layers, with the phenyl rings of the anilinium ions also being mutually perpendicular. The -NH$_3$ groups are hydrogen bonded to the out-of-plane chloride ligands, and the interplanar separations are determined by substituents on the phenyl ring.[2]

Compounds with unusual formulations have been encountered in this research,[2] and studies described here on the title compound, (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, revealed the presence of the first discrete CuCl$_6^{4-}$ complex. Characterization of this new, unexpected complex by single-crystal X-ray diffraction studies and by magnetic methods are discussed in this Article.

Experimental Section

Synthesis. To 15.2 mL (0.15 mol) of 3-chloroaniline (Aldrich Chemical Co.) and 28.73 g (0.17 mol) of copper(II) chloride dihydrate were added approximately 150 mL of distilled water and 350 mL of concentrated hydrochloric acid. The resulting solution was heated, with stirring, to the boiling point. The solution was then allowed to cool, and copious quantities of yellow crystals deposited. The crystals were collected on a glass-frit funnel and were washed with anhydrous diethyl ether. Anal. Calcd. for C$_{48}$H$_{56}$Cl$_{18}$CuN$_8$: C, 39.85; H, 3.90; Cl, 44.11; Cu, 4.39; N, 7.75. Found: C, 39.78; H, 3.88; Cl, 44.61; Cu, 4.32; N, 7.60. The compound decomposes slowly with one product being a black material.

Magnetic and Spectral Measurements. Magnetic susceptibility data from 4.4 to 22 K were collected by using a Princeton Applied Research Model 155 Foner vibrating sample magnetometer using procedures that have been described earlier.[4] The magnetometer was calibrated with HgCo(NCS)$_4$.[5,6] Samples of the standard and the compound under study were contained in precision milled Lucite sample holders. Approximately 150 mg of each were used. The magnetic susceptibility at room temperature was determined by the

Faraday method by using procedures described earlier.[7] A correction for the diamagnetism of the constituent atoms were estimated from Pascals constants.[8,9]

Electron paramagnetic resonance spectra at X-band frequency of single crystal and powdered samples were recorded with Varian Instruments E109 and E3 EPR spectrometers. The microwave frequency was monitored with a 5340 A Hewlett Packard frequency counter and diphenylpicrylhydrazyl (DPPH) was used as the field marker.

Crystallographic Data Collection. X-ray diffraction data were collected by using an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and by using molybdenum radiation at room temperature. Cell dimensions were obtained by least-squares fitting from 25 reflections with 2θ in the range $30.00°$ to $35.00°$. Of the 5510 unique reflections recorded in the range $2° < 2\theta < 50°$, 3825 reflections having $I > 2.5\sigma(I)$ were used in the structure determination. Data were corrected for Lorentz, polarization and absorption effects.

Refinement of the Structure. The positions of the copper and chlorine atoms were determined by direct methods after which the other atoms were located from difference syntheses. The structure was refined by full-matrix least squares, scattering factors were obtained[10], and corrected for anomalous dispersion. In the final cycles, a weighting scheme based on counter statistics was applied. All the non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters based on the atom to which they were attached.

An isotropic secondary extinction correction was made. Attempts
to refine the structure in space group P1 lead to no improvement
in the agreement factors indicating that P$\bar{1}$ was the correct choice.
All calculations were made using the NRCVAX suite of programs.[11]
Pertinent crystal data, details of data collection, and refinement
parameters are summarized in Tables I and SI (supplementary
material). Atomic positions, bond lengths, and bond angles are
given in Tables II-IV, SIII-SVI.

Results

Description of the Structure. The structure of (3-
chloroanilinium)$_8$[CuCl$_6$]Cl$_4$ consists of discrete 3-chloroanilinium
cations, discrete CuCl$_6^{4-}$ anions shown in Figure 1, and
uncoordinated chloride ions. The cations have no unique structural
features, and the bond angles and bond distances are given in
Tables SIV and SV. The substituted phenyl ring is nearly perfectly
planar, as shown by the torsional angles in Table SVI
(supplementary material), and the chloro substituent and the
nitrogen atom of the protonated-amino group lie in the plane. A
stereo-view of the packing of the chloroanilinium ions, the CuCl$_6^{4-}$
ions, and the uncoordinated chloride ions is given in Figure 2.

The coordination about the discrete [CuCl$_6$]$^{4-}$ ion in (3-
chloroanilinium)$_8$[CuCl$_6$]Cl$_4$ is that of a tetragonally compressed
octahedron with bond distances Cu-Cl(1) = 2.2773(11) Å, Cu-Cl(2)
= 2.6061(18) Å, and Cu-Cl(3) = 2.6086(20) Å. The Cl(1)-Cu-Cl(1a),
Cl(2)-Cu-Cl(2a), and Cl(3)-Cu-Cl(3a) angles are strictly 180°, and

the 12 remaining Cl(i)-Cu-Cl(j) angles differ from 90° by only 0.4 to 1.0°. See Figure 1 for the labels for the atoms and Tables III and IV for detailed metrical data that confirm the characterization of the $CuCl_6^{4-}$ ion as being a tetragonally compressed octahedron.

Magnetic Susceptibility. Magnetic susceptibility data were collected at room temperature and as a function of temperature in the range 4.4 to 22 K. The latter data are shown in Figure 3. The magnetic moment was found to be 1.8 B.M. at 290 K, 1.3 B.M. at 20 K and 0.6 B.M. at 4.4 K. There is a maximum in the magnetic susceptibility near 10 K. These data indicate that there are antiferromagnetic interactions in the compound. Since the material is magnetically dilute (1 spin/1447 amu), and the vibrating sample magnetometer is not exceptionally sensitive, the accuracy of the data is low. However, the data are adequate to assess the nature of the antiferromagnetic interactions, and to reveal the low-dimensional character of those interactions.

Inspection of the structure reveals that the $CuCl_6^{4-}$ units are arranged into chains along the a axis with a copper-copper separation of 8.55 Å. The copper-chloride bond distance along this direction is 2.28 Å, and the chloride-chloride separation is 3.99 Å. While chloride-chloride separations of this length would normally be considered rather long in view of the van der Waals radius of Cl being 1.80 Å as given by Pauling,[12] Brown and coworkers[13] found Heisenberg chain properties with $J = -7.6$ cm^{-1} in chains of $[CuCl_2(AdH^+)_2]Cl_2$ (AdH$^+$ is protonated adenine) with a

similar Cu-Cl⋯Cl-Cu superexchange pathway. The chloride-chloride separations in $[CuCl_2(AdH^+)_2]Cl_2$ are 3.76 Å. Also, Hatfield and Jones[14] have reported significant antiferromagnetic interactions in $[Co(NH_3)_6][CuCl_5]$. The chloride-chloride contacts between monomeric $[CuCl_5]^{3-}$ ions in this latter compound are 4.11 Å.

Assuming isotropic exchange, the exchange Hamiltonian for a linear chain compound is

$$H_{ex} = -2J_{ij}\Sigma_{i \leq j}\ \mathbf{S}_i \cdot \mathbf{S}_j$$

with $S_i = S_j = 1/2$. Bonner and Fisher[15] showed that the maximum magnetic susceptibility and the temperature at which it occurs, are uniquely defined by

$$k_B T_{max}/|J| = 1.282$$

and

$$X_{max}|J|/Ng^2\mu_B^2 = 0.07346$$

Hall[16] has provided the following analytical expression for the temperature variation of the magnetic susceptibility of antiferromagnetic Heisenberg chains with S = 1/2:

$$X_{BF} = (Ng^2\mu_B^2/k_BT)[A + Bx + Cx^2]/[1 + Dx + Ex^2 + Fx^3]$$

where A = 0.25, B + 0.14995, C = 0.30094, D = 1.9862, E = 0.68854, F = 6.0626 and $x = |J|/k_BT$. Interchain interactions were accounted for by inclusion of a molecular field correction term:

$$X_{corr} = X_{BF}/(1 - 2zJ'X_{BF}/Ng^2\mu_B^2)$$

where J' is the interchain exchange parameter and z is the number of nearest neighbors. A least-squares fit of the magnetic susceptibility equation to the data using a non-linear Simplex fitting routine[17,18] yielded J = -5.6 cm⁻¹, g = 2.0, and J' = -2.1 cm⁻¹.

The solid line shown in Figure 3 was generated with these best-fit parameters. Although there are large experimental uncertainties in the g value and the interchain mean-field parameter J', the intrachain exchange coupling constant agrees well with that predicted from the expression $k_B T_{max}/|J| = 1.282$. When T_{max} is taken to be 10 K, a value for $|J|$ of 5.4 cm^{-1} results.

Electron Paramagnetic Resonance Spectra. EPR spectra collected on a single crystal of (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, as well as on a powdered sample of the compound, are shown in Figures 4 and 5. To verify the identity of the crystal used for the EPR experiment, a small part of the crystal was cut away, and the unit cell of the fragment was determined to be identical to that of the crystal used for the X-ray structural determination. This experiment also confirms that the crystal used in the X-ray structural determination is characteristic of the bulk sample.

The single crystal EPR spectra clearly is of the "reversed" nature expected for a compressed octahedron with a ^2A ground state. Analysis of the spectral features yield $g_\parallel = 2.06$ and $g_\perp = 2.19$. Although $g_\parallel$ should be equal to 2.0 for a tetragonally-compressed six-coordinate copper(II) complex in a high symmetry environment,[19] there are two mechanisms that contribute to the departure of $g_\parallel$ from 2.0 in (3-chloroanilinium)[CuCl$_6$]Cl$_4$. The copper ion sits only on a center of inversion in this complex, and it is possible for excited states with orbital angular momentum to be mixed into the ground state. Since the departure of $g_\parallel$ from 2.0 is small,

being only 0.06, the amount of admixture of excited states into the ground state must be small. The second mechanism which can cause a departure from $g_{\parallel}$ = 2.0 involves the dynamic Jahn-Teller effect.[20]

The expression for $g_{\perp}$ (in high symmetry) is

$$g_{\perp} = 2.0023 - 6\lambda/\Delta E(d_z2 \rightarrow d_{xz},d_{yz})$$

Although the $d_z2 \rightarrow d_{xz},d_{yz}$ band was not identified in the electronic spectrum, it is expected to be at a low energy as a consequence of the long bond distances and resulting small ligand field splitting. Thus, $g_{\perp}$ is expected to depart substantially from the free electron value.

Discussion

In the course of research on substituted anilinium chlorocuprates,[2] compounds with unusual formulations have been encountered. For the most part, these have been only partially characterized, since the focus of prior research has been the identification of planar chlorocuprate networks with intercalated anilinium cations. The cations that had been studied were limited to those with substituents in the para-position of the phenyl ring, since substituents in this position were thought to be most effective in modulating the interplanar separation.

Continuation of this research with anilinium cations having substituents in other ring positions have revealed a compound formulated, from analytical data, as (3-chloroanilinium)$_8$CuCl$_{10}$. The compound is not very stable. A sample stored on the bench top in a beaker covered with Parafilm® began to turn black after several

weeks. An EPR spectrum of a powdered sample, collected several months after its synthesis, revealed numerous additional lines from decomposition products.

A single crystal X-ray structure determination on (3-chloroanilinium)$_8$CuCl$_{10}$ revealed the presence of 3-chloroanilinium ions, CuCl$_6^{4-}$ units, and uncoordinated chloride ions. A stereo-view which shows the arrangement of these ions in the unit cell is given in Figure 2. The structure of the hexachlorocuprate(II) ion is of especial interest. There are no prior examples of a discrete CuCl$_6^{4-}$ ion. In fact, it was thought for a long time, that only large like-charged counterions, could stabilize hexachlorometallates in the solid state,[21] although recent work has revealed such complexes with small cations.[22]

It is very common for hexa-coordinated copper(II) complexes to exhibit 4 + 2 coordination as a result of the Jahn-Teller effect, with the distortion resulting in four short copper-ligand bonds and two long copper-ligand bonds. There appears to be only one other example of a CuL$_6^{q+}$ axial compression, that being the CuF$_6^{4-}$ ion in Ba$_2$CuF$_6$.[23] Burdett[23] notes that even the ZnF$_6^{4-}$ ion in Ba$_2$ZnF$_6$ is octahedrally compressed, and he attributes this, and the compression of the CuF$_6^{4-}$ ion in Ba$_2$CuF$_6$, to lattice forces, and not to the Jahn-Teller effect. An early report[24] that K$_2$CuF$_4$ contained axially compressed hexafluorocuprate entities was later shown to be incorrect.[25]

The magnetic orbital for the compressed octahedral copper(II) ion is d_{z^2}. The compressed copper-chloride bonds occur along the

a axis of the crystal and are aligned one-dimensionally such that a Cu-Cl$\cdots$Cl-Cu exchange pathway exists, see Figure 2 for the pathway and Figure 6 for the superexchange orbitals. This relatively long superexchange pathway allows the antiferromagnetic interactions between copper ions. The question arises as to whether the packing of the $CuCl_6^{4-}$ ions in the crystal structure leads to the axial compression. This appears to be unlikely since the chloride-chloride contact between $CuCl_6^{4-}$ ions of 3.99 Å is 0.23 Å longer than the chloride-chloride contact in $[CuCl_2(AdH^+)_2]Cl_2$, yet the copper-chloride separation of 2.29 Å in $[CuCl_2(AdH^+)_2]Cl_2$ is typical of copper-chloride bonds in tetrahedrally coordinated copper(II). For example, the average copper-chloride bond distance in the flattened tetrahedron $CuCl_4^{2-}$ in Cs_2CuCl_4 is 2.2 Å.[26,27]

The EPR spectra agrees with tetragonal compression since the relative positions of $g_{\perp}$ and $g_{\parallel}$ are those expected for an axially compressed octahedron. These are reversed from those predicted and observed for tetragonal elongation normally seen in 4 + 2 coordinated copper(II) systems. "Reversed" EPR spectra arising from d_{z^2} ground states occur in copper(II) complexes having trigonal bipyramidal, tetragonally compressed octahedral, cis-distorted octahedral, and rhombic distorted octahedral stereochemistries. Such reversed spectra may also arise for certain orientations of tetragonally elongated octahedral species where the observed crystal g values $g_{\parallel}'$ and $g_{\perp}'$ are related to the site g values by the relationships

$$g_{\parallel}'^2 = g_{\perp}^2$$

and

$$g_{\perp}'^2 = g_{\perp}^2 \cos^2\alpha + g_{\parallel}^2 \sin^2\alpha$$

where 2α is the angle between the tetragonal axes. Misalignment of molecular tetragonal axes will yield a unique perpendicular resonance occurring at high field, and a more intense resonance at a lower field which is an average of molecular parallel and perpendicular g values. However, such is not the case for the $CuCl_6^{4-}$ ion in (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$. This is a _bona fide_ case of a "reversed" EPR spectrum arising from a d_z2 ground state in a tetragonally compressed octahedron.

Acknowledgement

Supplementary Material Available. Figure of the 3-chloroanilinium cation (1 page), tables of crystallographic data collection details (Table SI, 1 page), anisotropic thermal parameters (SII, 2 pages), a complete list of atomic parameters including hydrogen atom coordinates (SIII, 1 page), a complete list of bond angles (SIV, 1 page), a complete list of bond distances (SV, 1 page), phenyl ring torsion angles (SVI, 1 page), and calculated and observed structure factors (SVII, 26 pages). Ordering information is given on any current masthead page.

References

(1)   Department of Education Fellow

(2)   Hatfield, W. E., unpublished observations.

(3)   Larsen, K. P. Acta Chem. Scand. 1974, A28, 194.

(4)   Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield,
      W. E. Inorg. Chem. 1980, 19, 1297.

(5)   Figgis, B. N.; Nyholm, R. S. J. Chem. Soc. 1958, 4190.

(6)   Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield,
      W. E. J. Phys. Chem. 1977, 81, 1303.

(7)   Helms, J. H.; ter Haar, L. W.; Hatfield, W. E.; Harris, D.
      L.; Jayaraj, K.; Toney, G. E.; Gold, A.; Mewborn, T. D.;
      Pemberton, J. R. Inorg. Chem. 1986, 25, 2334.

(8)   Figgis, B. N.; Lewis, J. In Modern Coordination Chemistry;
      Lewis, J. and Wilkins, R. L., Eds.; New York: Interscience;
      1960; Chap. 6.

(9)   Weller, R. R.; Hatfield, W. E. J. Chem. Ed. 1979, 56, 652.

(10) International Tables for X-ray Crystallography, 1974, Vol.
      IV, Kynoch Press, Birmingham.

(11) Gabe, E.J.; Page, Y Le; Charland, J.P.; Lee, F.L.; White,
      P.S. J. Appl. Crystallography, 1989, 22, 384-387.

(12) Pauling, L. The Nature of the Chemical Bond, 3rd Ed.; Cornell
      University Press:Ithaca, New York; 1960; p. 260.

(13) Brown, D. B.; Hall, J. W.; Helis, H. M.; Walton, E. G.;
      Hodgson, D. J.; Hatfield, W. E. Inorg. Chem. 1977, 16, 2675.

(14) Hatfield, W. E.; Jones, E. R. Inorg. Chem. 1970, 9, 1502.

(15) Bonner, J. C.; Fisher, M. E. Phys. Rev. A 1964, 135, 640.

(16) Hall, J. W.; Ph. D. Dissertation; University of North
      Carolina, 1977.

(17) Spendley, W.; Hext, G. R.; Himsworth, F. R. Technometrics
      1962, 4, 441.

(18) Nelder, J. A.; Mead, R. Comput. J. 1965, 7, 308.

(19) Hathaway, B. J.; Billing, D. E. Coord. Chem. Rev. 1970, 5,
      143.

(20) Abragam, A.; Bleaney, B. Electron Paramagnetic Resonance of
      Transition Ions 1970, 464.

(21) Hatfield, W. E.; Fay, R. C.; Pfluger, C. E.; Piper, T. S.
      J. Am. Chem. Soc. 1963, 85, 265.

(22) Beattie, J. K.; Moore, C. J. Inorg. Chem. 1982, 21, 1292.

(23) Burdett, J. K. Inorg. Chem. 1981, 20, 1959.

(24) Knox, K. J. Chem. Phys. 1959, 30, 991.

(25) Haegele, R.; Babel, D. Z. anorg. allg. Chem. 1974, 409, 11.

(26) Helmholz, L.; Kroh, R. F. J. Am. Chem. Soc. 1952, 74, 1176.

(27) Morosin, B.; Lingafelter, E. C. J. Phys. Chem. 1961, 65, 50.

Table I. Crystallographic Data
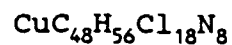
$CuC_{48}H_{56}Cl_{18}N_8$ fw = 1446.71

$\underline{a}$ = 8.5488(16) Å   space group P$\bar{1}$

$\underline{b}$ = 13.964(6) Å   T ≈ 20°C

$\underline{c}$ = 14.273(7) Å λ = 0.70930 Å

α = 90.46(4)° ρ_{calcd} = 1.519 g cm^{-3}

β = 107.82(3)° μ = 1.15 mm^{-1}

γ = 102.11(3)°   trans. coeff. = 0.740 - 0.743

V = 1581.2(10) Å^3 extinction coeff. = 0.024(28)

Z = 1

R(F) = 0.044

R_w(F)= 0.053

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$

Table II.   Atomic Parameters x, y, z and B_{iso}.

	x	y	z	B_{iso}
Cu1	0	0	0	2.79(3)
Cl1	0.26796(12)	0.00195(7)	0.00183(7)	2.77(4)
Cl2	-0.03272(14)	-0.18135(10)	0.04728(8)	4.55(6)
Cl3	0.11512(15)	0.06467(9)	0.18576(10)	4.71(6)
Cl4	0.35229(15)	0.91226(8)	0.74527(8)	4.00(5)
Cl5	0.53238(15)	0.24580(8)	0.92576(8)	3.96(6)
Cl11	1.01872(25)	0.41516(10)	0.88578(12)	7.26(10)
N11	1.1605 (5)	0.7921 (3)	0.8889 (3)	3.99(19)
C11	0.9901 (6)	0.5236 (3)	0.8316 (4)	4.3 (3)
C12	1.0873 (6)	0.6120 (3)	0.8816 (3)	3.70(22)
C13	1.0620 (5)	0.6965 (3)	0.8369 (3)	3.24(20)
C14	0.9450 (8)	0.6950 (4)	0.7461 (4)	5.7 (3)
C15	0.8541 (9)	0.6049 (5)	0.6991 (4)	7.4 (4)
C16	0.8740 (7)	0.5191 (4)	0.7415 (4)	5.7 (3)
C121	0.49084(20)	0.36603(11)	0.55581(11)	6.08(7)
N21	0.6597 (5)	0.1066 (3)	0.7981 (3)	3.97(19)
C21	0.5615 (6)	0.2591 (3)	0.5840 (3)	3.93(21)
C22	0.5865 (5)	0.2284 (3)	0.6786 (3)	3.29(20)
C23	0.6365 (5)	0.1417 (3)	0.6985 (3)	3.19(19)
C24	0.6637 (6)	0.0854 (4)	0.6277 (4)	4.28(23)
C25	0.6396 (7)	0.1180 (4)	0.5350 (4)	5.1 (3)
C26	0.5896 (7)	0.2043 (4)	0.5124 (3)	4.9 (3)
C131	0.13042(18)	0.11746(10)	0.42803(9)	5.18(7)
N31	0.2027 (5)	0.0929 (3)	0.7967 (3)	4.08(20)

C31	0.1124 (6)	0.1607 (3)	0.5381 (3)	3.53(20)
C32	0.1627 (5)	0.1101 (3)	0.6210 (3)	3.43(20)
C33	0.1509 (5)	0.1462 (3)	0.7076 (3)	3.33(19)
C34	0.0912 (6)	0.2296 (3)	0.7133 (3)	4.21(24)
C35	0.0409 (7)	0.2777 (4)	0.6287 (4)	4.7 (3)
C36	0.0525 (6)	0.2438 (3)	0.5407 (3)	4.28(24)
C141	0.20774(21)	0.54335(11)	0.59506(11)	6.81(8)
N41	0.5981 (4)	0.7879 (3)	0.8834 (3)	3.98(18)
C41	0.3545 (6)	0.5691 (3)	0.7116 (3)	4.12(22)
C42	0.4168 (6)	0.6653 (3)	0.7488 (3)	3.58(21)
C43	0.5347 (5)	0.6853 (3)	0.8416 (3)	3.45(20)
C44	0.5896 (7)	0.6122 (4)	0.8969 (4)	4.9 (3)
C45	0.5252 (8)	0.5161 (4)	0.8573 (4)	5.8 (3)
C46	0.4087 (7)	0.4943 (3)	0.7653 (4)	5.4 (3)

B_{iso} is the Mean of the Principal Axes of the Thermal Ellipsoid

Table III. Bond Lengths (A) about Copper

Cu (1) - Cl (1)	2.2773 (11)
Cu (1) - Cl (1) a	2.2773 (11)
Cu (1) - Cl (2)	2.6061 (18)
Cu (1) - Cl (2) a	2.6061 (18)
Cu (1) - Cl (3)	2.6086 (20)
Cu (1) - Cl (3) a	2.6086 (20)

Table IV.   Bond Angles (in degrees) About Copper

Cl (1) - Cu (1) - Cl (1) a	180.0
Cl (1) - Cu (1) - Cl (2)	89.46 (5)
Cl (1) - Cu (1) - Cl (2) a	90.54 (5)
Cl (1) - Cu (1) - Cl (3)	89.60 (5)
Cl (1) - Cu (1) - Cl (3) a	90.40 (5)
Cl (1) a - Cu (1) - Cl (2)	90.54 (5)
Cl (1) a - Cu (1) - Cl (2) a	89.46 (5)
Cl (1) a - Cu (1) - Cl (3)	90.40 (5)
Cl (1) a - Cu (1) - Cl (3) a	89.60 (5)
Cl (2) - Cu (1) - Cl (2) a	180.0
Cl (2) - Cu (1) - Cl (3)	91.04 (5)
Cl (2) - Cu (1) - Cl (3) a	88.96 (5)
Cl (2) a - Cu (1) - Cl (3)	88.96 (5)
Cl (2) a - Cu (1) - Cl (3) a	91.04 (5)
Cl (3) - Cu (1) - Cl (3) a	180.0

Figure Captions

Figure 1. Ortep diagram of $CuCl_6^{4-}$ anion. The compressed axis is composed of the Cl(1)-Cu-Cl(1a) bonds.

Figure 2. A stereo-view which shows the packing of the ions in the unit cell.

Figure 3. Magnetic susceptibility data in the range 4 to 22 K. Experimental data are given as +'s, and the solid line is the best fit of antiferromagnetic Heisenberg chain theory to the data with the parameters given in the text.

Figure 4. EPR spectrum of a single crystal of (3-chloro-anilinium)$_8$CuCl$_{10}$ oriented with the $\underline{a}$ axis perpendicular to the magnetic field. The single crystal value of $g_\perp$ is 2.186. The feature observed in the 10-fold magnification is $g_{||}$ (from misaligned fragments) of 2.062. The standard, DPPH radical, has a g value of 2.002.

Figure 5. The powder EPR spectrum of (3-chloroanilinium)$_8$CuCl$_{10}$. The resonance arising from $g_\perp$ is at the lowest magnetic field with the resonance at the highest field arising from DPPH.

Figure 6. The superexchange orbitals in the Cu-Cl$\cdots$Cl-Cu pathway.
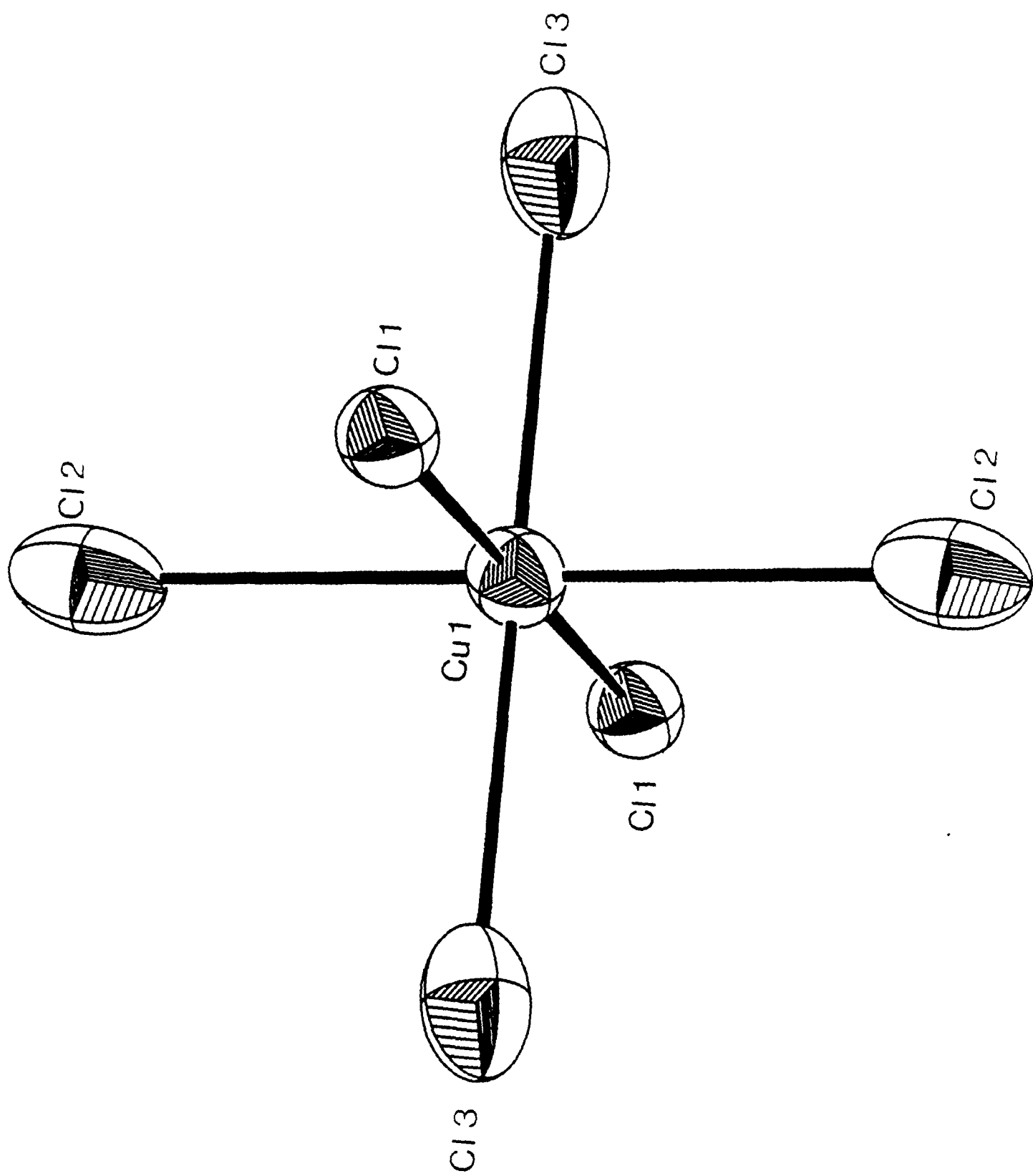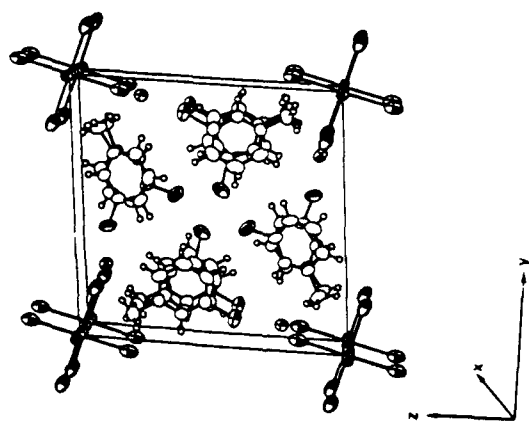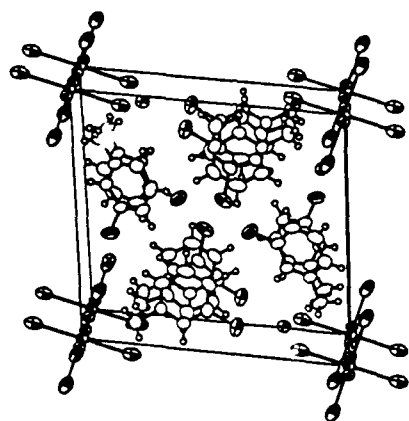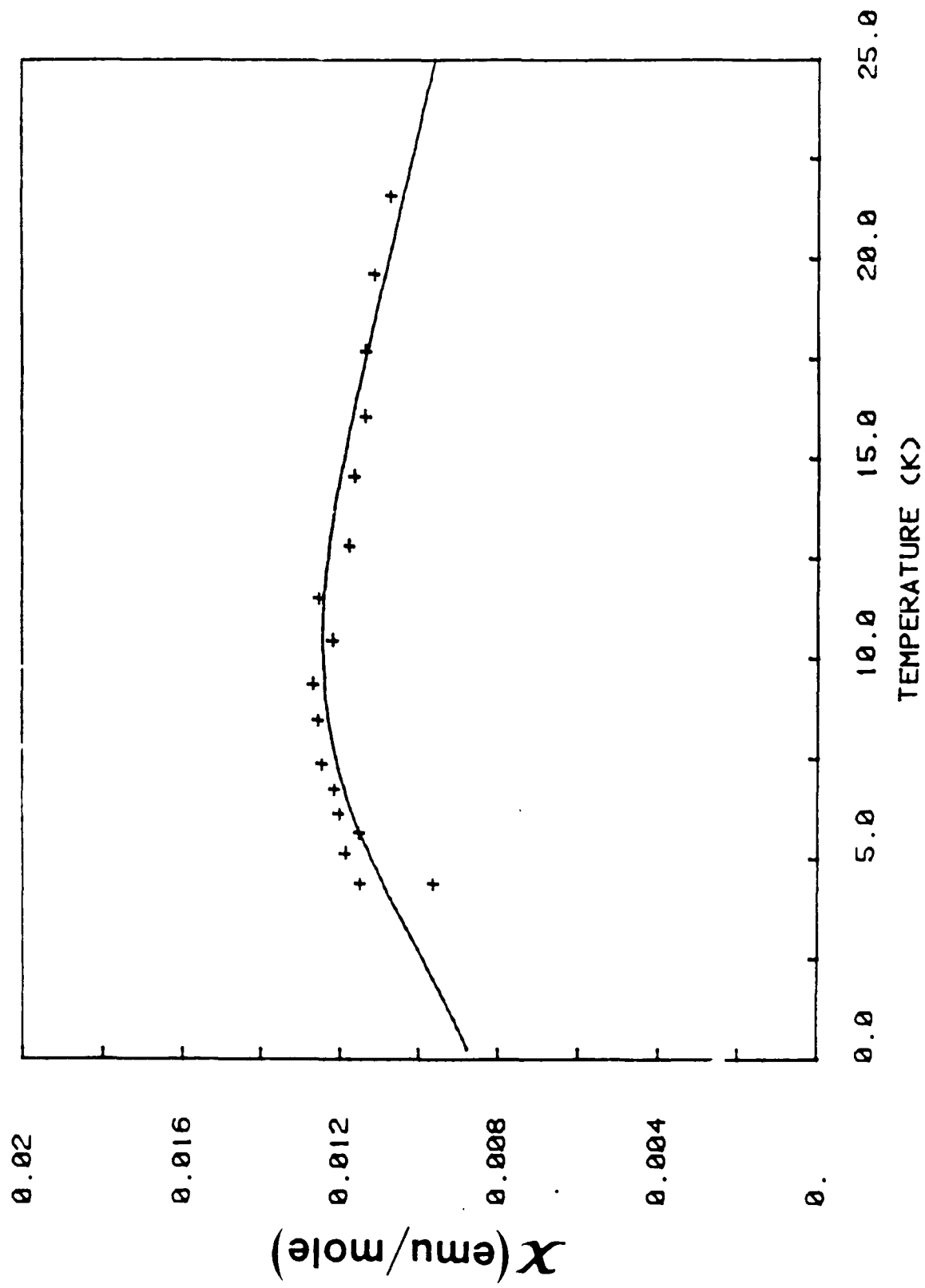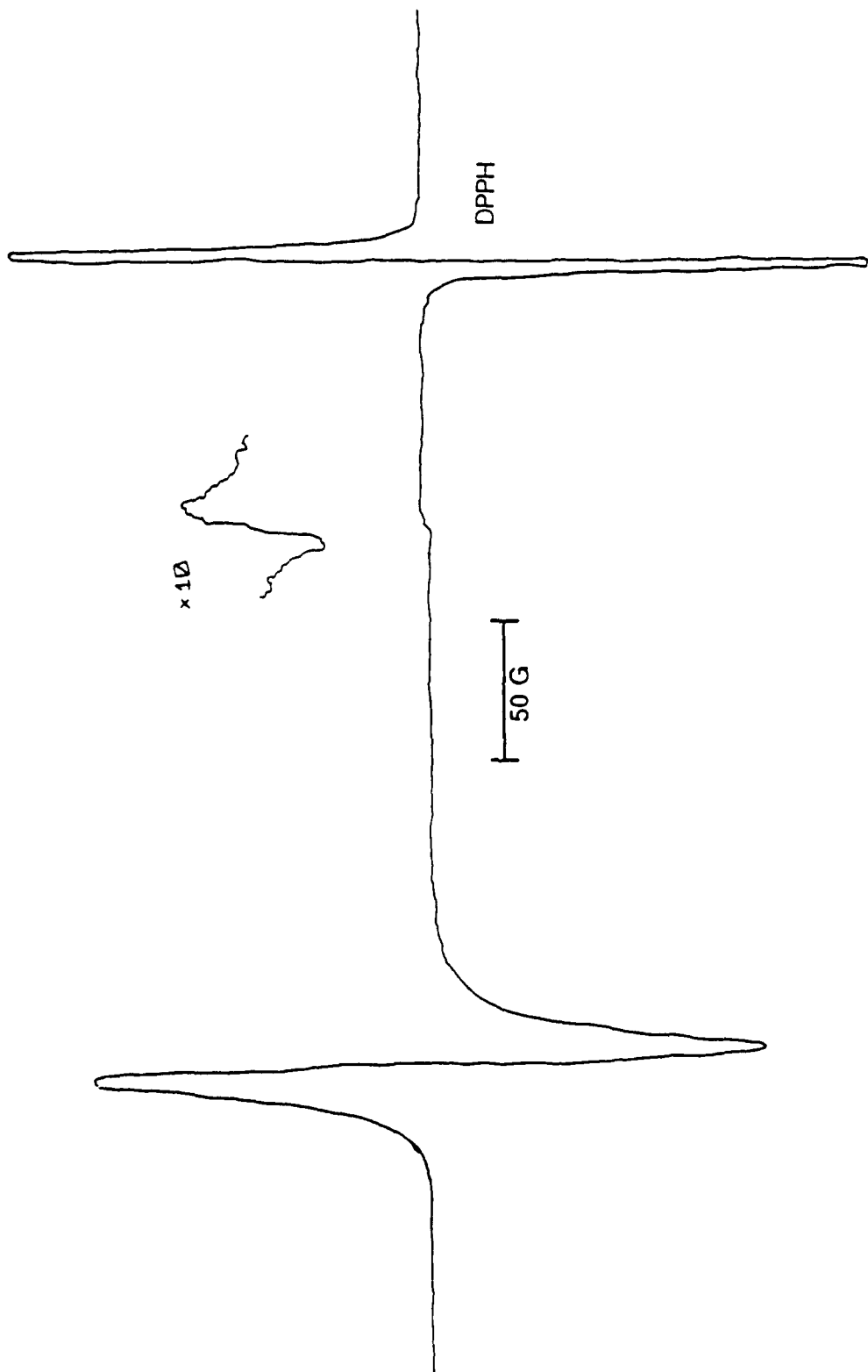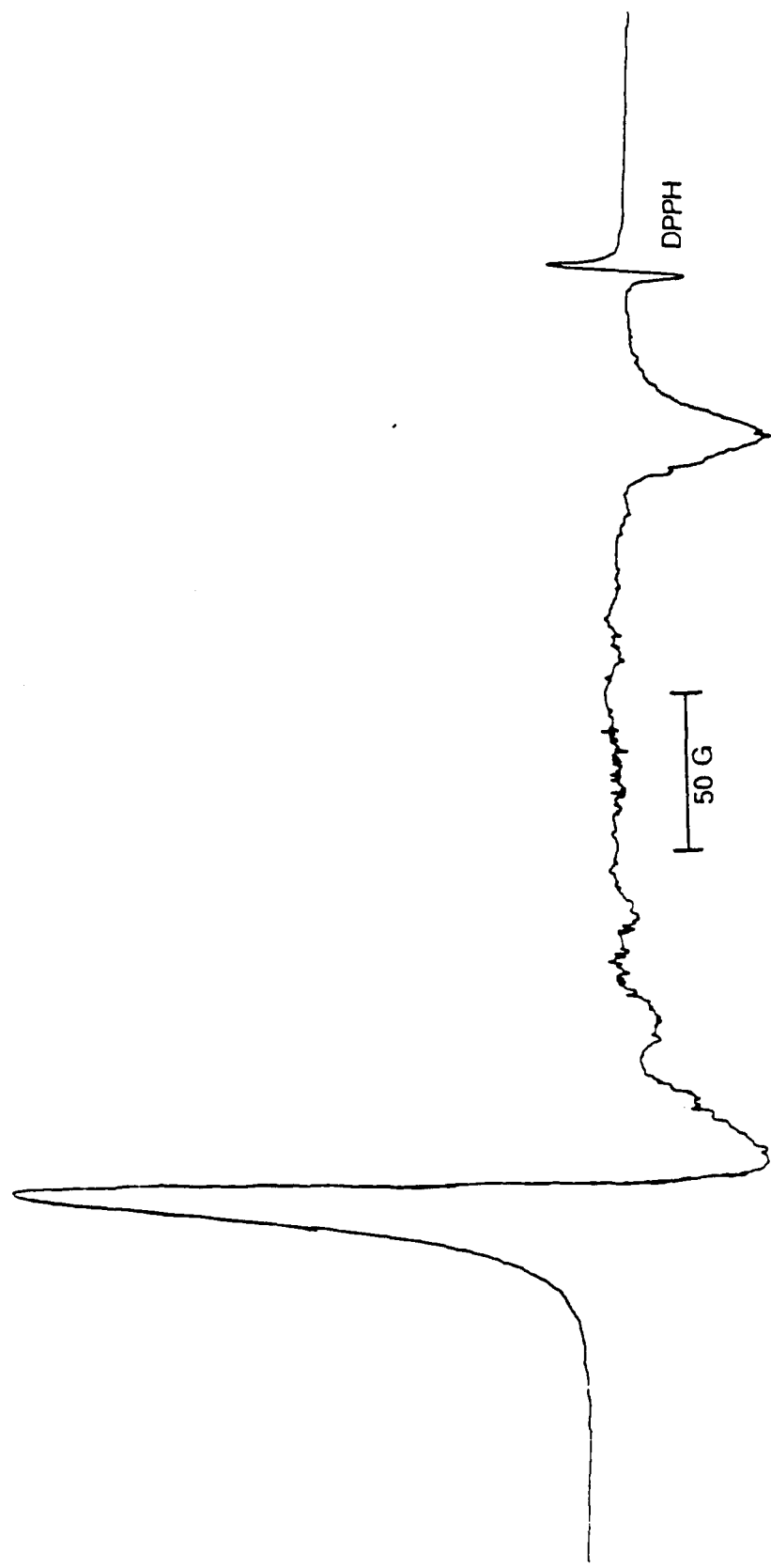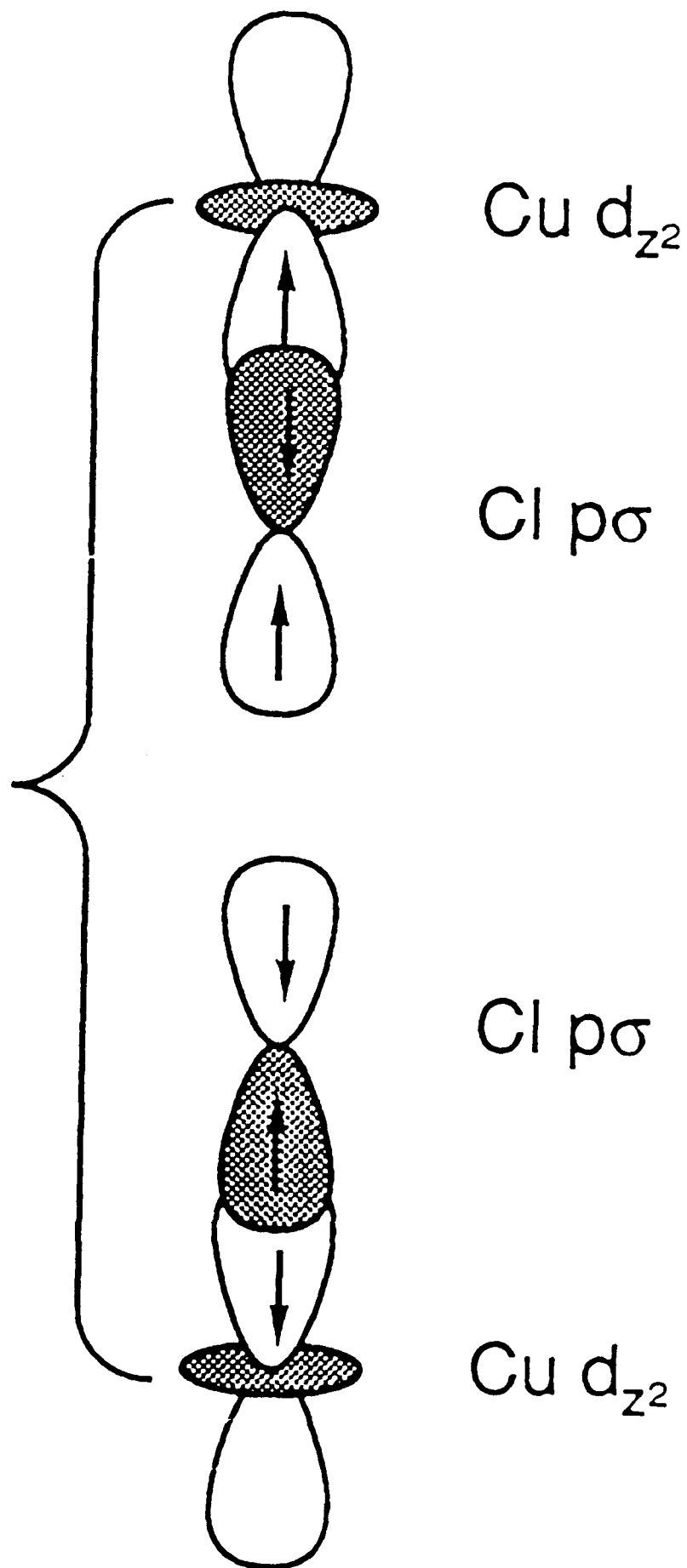
χ (emu/mole)

0.02 0.016 0.012 0.008 0.004 0.

0.0 5.0 10.0 15.0 20.0 25.0

TEMPERATURE (K)

DPPH

×10

50 G

Cu d$_{z^2}$

Cl pσ

a = 8.55 Å

Cl pσ

Cu d$_{z^2}$

Identification of a Novel Tetragonally-Compressed Six-Coordinate

Copper(II) Complex: Preparation and Characterization of a

3-Chloroanilinium Copper Chloride Complex

$(3\text{-chloroanilinium})_8[CuCl_6]Cl_4$

Denise A. Tucker, Peter S. White, Kathleen L. Trojan,

Martin L. Kirk and William E. Hatfield

SUPPLEMENTARY MATERIAL

Figure SI. Ortep diagram of anilinium cation.
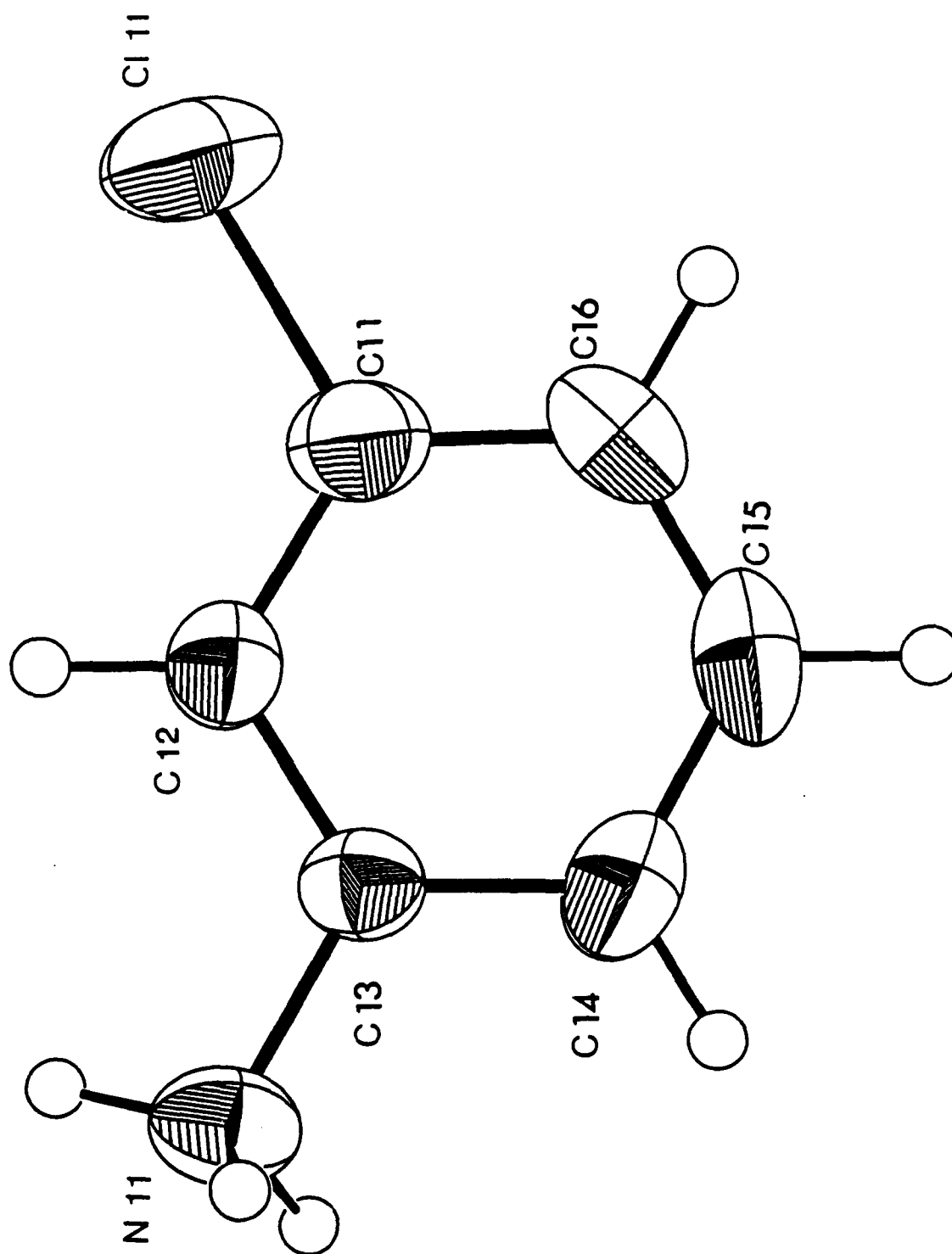
Space Group and Cell Dimensions   Triclinic,   P -1
a 8.5488(16)   b 13.964(6)   c 14.273(7)
alpha 90.46(4)   beta 107.82(3)   gamma 102.11(3)
        Volume 1581.2(10)A**3

Empirical formula : Cu Cl18 C48 H56 N8

Cell dimensions were obtained from 25 reflections with 2Theta angle
in the range 30.00 - 35.00 degrees.

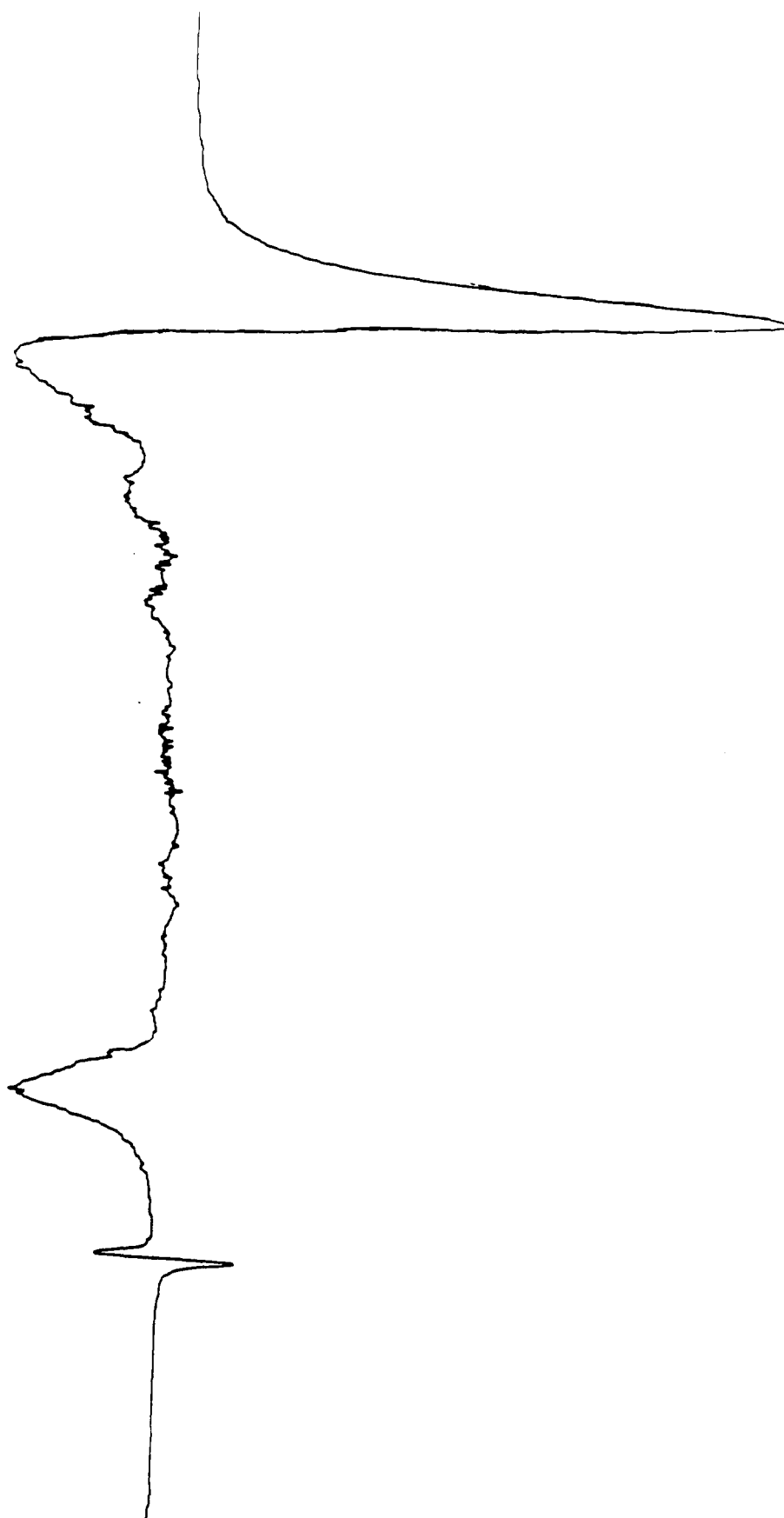Crystal dimensions : 0.30 X 0.30 X 0.45 mm, fragment cut from larger needl.

FW =   1446.71   Z =   1   F(000) =   735

Dcalc 1.519Mg.m-3, mu   1.15mm-1, lambda 0.70930A, 2Theta(max) 50.0

The intensity data were collected on a Nonius diffractometer,
using the theta/2theta scan mode.
The h,k,l ranges are :--   -10   9,   0 16,   -16 16
No. of reflections measured   5918
No. of unique reflections   5510
No. of reflections with Inet > 2.5sigma(Inet) 3825
Absorption corrections were made.
The minimum and maximum transmission factors are 0.740828 and 0.742505.
[Only an approximate spherical correction]

The last least squares cycle was calculated with
 66 atoms, 341 parameters and 3825 out of 5510 reflections.
Weights based on counting-statistics were used.
The weight modifier K in KFo**2 is 0.000500

The residuals are as follows :--
For significant reflections, RF 0.044, Rw 0.053 GoF 1.59
For all reflections,   RF 0.072, Rw 0.074.
where RF = Sum(Fo-Fc)/Sum(Fo),.
     Rw = Sqrt[Sum(w(Fo-Fc)**2)/Sum(wFo**2)] and
    GoF = Sqrt[Sum(w(Fo-Fc)**2)/(No. of reflns - No. of params.)]
The maximum shift/sigma ratio was 0.199.

In the last D-map, the deepest hole was -0.610e/A**3,
and the highest peak   0.580e/A**3.

Secondary ext. coeff. =   0.023971   sigma =   0.027892

Table of u(i,j) or U values (x 100).
e.s.d's. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
CU1	3.42(4)	3.83(4)	3.39(4)	1.03(3)	1.00(3)	0.49(3)
CL1	3.50(5)	3.73(5)	3.32(5)	1.01(4)	0.96(4)	0.40(4)
CL2	4.09(6)	8.89(9)	4.05(6)	1.07(6)	1.20(5)	-0.19(6)
CL3	5.19(7)	5.54(7)	8.40(9)	2.23(6)	3.16(7)	2.69(7)
CL4	5.77(7)	4.56(6)	4.58(6)	1.14(5)	1.22(6)	0.89(5)
CL5	6.01(7)	4.75(6)	3.88(6)	1.13(6)	1.00(5)	0.14(5)
CL11	13.53(15)	4.36(8)	8.93(11)	1.75(9)	2.59(11)	1.59(7)
N11	4.88(23)	4.13(22)	6.7 (3)	1.09(18)	2.51(20)	-0.06(19)
C11	6.5 (3)	4.2 (3)	5.5 (3)	1.13(24)	2.1 (3)	0.53(23)
C12	5.0 (3)	4.9 (3)	3.91(25)	1.28(22)	0.93(22)	0.41(21)
C13	4.6 (3)	3.65(24)	4.30(25)	0.95(20)	1.76(21)	0.23(19)
C14	9.1 (4)	6.5 (3)	4.9 (3)	2.5 (3)	0.1 (3)	1.3 (3)
C15	10.1 (5)	9.1 (5)	5.3 (4)	1.9 (4)	-2.7 (3)	-0.3 (3)
C16	7.3 (4)	5.5 (3)	6.3 (3)	-0.3 (3)	-0.2 (3)	-1.3 (3)
CL21	8.31(10)	6.92(9)	6.97(9)	2.47(8)	0.55(8)	3.05(7)
N21	4.41(22)	6.1 (3)	4.71(22)	1.96(19)	1.11(18)	1.92(19)
C21	4.3 (3)	5.8 (3)	3.86(25)	0.58(23)	0.25(21)	1.53(22)
C22	3.74(24)	4.9 (3)	3.56(23)	0.91(20)	0.79(19)	0.70(20)
C23	3.21(23)	4.8 (3)	3.78(24)	0.51(20)	0.81(19)	1.25(20)
C24	5.2 (3)	5.5 (3)	5.3 (3)	1.34(24)	1.12(24)	0.13(23)
C25	7.0 (4)	7.6 (4)	4.5 (3)	1.0 (3)	1.7 (3)	-0.9 (3)
C26	6.9 (3)	7.8 (4)	3.2 (3)	0.7 (3)	0.78(24)	1.10(24)
CL31	7.97(9)	7.91(9)	3.61(6)	2.17(8)	1.30(6)	0.81(6)
N31	4.44(23)	7.3 (3)	3.96(21)	1.53(20)	1.48(18)	2.02(19)

C31	4.2 (3)	5.2 (3)	3.38(23)	0.71(21)	0.54(20)	0.92(20)
C32	4.4 (3)	4.3 (3)	4.4 (3)	1.10(21)	1.26(21)	0.89(20)
C33	3.26(23)	5.0 (3)	3.77(24)	0.23(20)	0.68(19)	1.13(20)
C34	5.9 (3)	5.4 (3)	4.9 (3)	0.73(25)	2.29(25)	0.39(23)
C35	6.8 (3)	4.5 (3)	7.5 (4)	2.3 (3)	2.8 (3)	1.5 (3)
C36	6.1 (3)	5.2 (3)	4.7 (3)	1.44(25)	1.21(24)	1.77(23)
CL41	9.33(12)	7.53(10)	5.97(9)	-0.42(9)	-0.40(8)	-1.80(7)
N41	3.85(21)	4.75(22)	5.84(25)	0.41(18)	0.93(19)	-1.13(19)
C41	5.3 (3)	5.1 (3)	4.5 (3)	0.00(23)	1.21(23)	-1.06(22)
C42	4.6 (3)	4.4 (3)	4.3 (3)	0.47(21)	1.26(21)	0.22(20)
C43	3.77(25)	4.09(25)	5.0 (3)	0.19(20)	1.54(21)	-0.65(20)
C44	6.2 (3)	5.7 (3)	5.7 (3)	1.7 (3)	-0.1 (3)	0.0 (3)
C45	8.5 (4)	4.8 (3)	7.6 (4)	2.1 (3)	0.5 (3)	0.7 (3)
C46	8.4 (4)	3.4 (3)	8.1 (4)	0.3 (3)	2.6 (3)	-0.9 (3)

Anisotropic Temperature Factors are of the form
Temp=-2*Pi*Pi*(h*h*u11*astar*astar+---+2*h*k*u12*astar*bstar+---)

Table SIII. Atomic Parameters x,y,z

	x	y	z	Biso
CU1	0	0	0	2.79(3)
CL1	0.26796(12)	0.00195(7)	0.00183(7)	2.77(4)
CL2	-0.03272(14)	-0.18135(10)	0.04728(8)	4.55(6)
CL3	0.11512(15)	0.06467(9)	0.18576(10)	4.71(6)
CL4	0.35229(15)	0.91226(8)	0.74527(8)	4.00(5)
CL5	0.53238(15)	0.24580(8)	0.92576(8)	3.96(6)
CL11	1.01872(25)	0.41516(10)	0.88578(12)	7.26(10)
N11	1.1605 (5)	0.7921 (3)	0.8889 (3)	3.99(19)
C11	0.9901 (6)	0.5236 (3)	0.8316 (4)	4.3 (3)
C12	1.0873 (6)	0.6120 (3)	0.8816 (3)	3.70(22)
C13	1.0620 (5)	0.6965 (3)	0.8369 (3)	3.24(20)
C14	0.9450 (8)	0.6950 (4)	0.7461 (4)	5.7 (3)
C15	0.8541 (9)	0.6049 (5)	0.6991 (4)	7.4 (4)
C16	0.8740 (7)	0.5191 (4)	0.7415 (4)	5.7 (3)
CL21	0.49084(20)	0.36603(11)	0.55581(11)	6.08(7)
N21	0.6597 (5)	0.1066 (3)	0.7981 (3)	3.97(19)
C21	0.5615 (6)	0.2591 (3)	0.5840 (3)	3.93(21)
C22	0.5865 (5)	0.2284 (3)	0.6786 (3)	3.29(20)
C23	0.6365 (5)	0.1417 (3)	0.6985 (3)	3.19(19)
C24	0.6637 (6)	0.0854 (4)	0.6277 (4)	4.28(23)
C25	0.6396 (7)	0.1180 (4)	0.5350 (4)	5.1 (3)
C26	0.5896 (7)	0.2043 (4)	0.5124 (3)	4.9 (3)
CL31	0.13042(18)	0.11746(10)	0.42803(9)	5.18(7)
N31	0.2027 (5)	0.0929 (3)	0.7967 (3)	4.08(20)
C31	0.1124 (6)	0.1607 (3)	0.5381 (3)	3.53(20)
C32	0.1627 (5)	0.1101 (3)	0.6210 (3)	3.43(20)
C33	0.1509 (5)	0.1462 (3)	0.7076 (3)	3.33(19)
C34	0.0912 (6)	0.2296 (3)	0.7133 (3)	4.21(24)
C35	0.0409 (7)	0.2777 (4)	0.6287 (4)	4.7 (3)
C36	0.0525 (6)	0.2438 (3)	0.5407 (3)	4.28(24)
CL41	0.20774(21)	0.54335(11)	0.59506(11)	6.81(8)
N41	0.5981 (4)	0.7879 (3)	0.8834 (3)	3.98(18)
C41	0.3545 (6)	0.5691 (3)	0.7116 (3)	4.12(22)
C42	0.4168 (6)	0.6653 (3)	0.7488 (3)	3.58(21)
C43	0.5347 (5)	0.6853 (3)	0.8416 (3)	3.45(20)
C44	0.5896 (7)	0.6122 (4)	0.8969 (4)	4.9 (3)
C45	0.5252 (8)	0.5161 (4)	0.8572 (4)	5.8 (3)
C46	0.4087 (7)	0.4943 (3)	0.7653 (4)	5.4 (3)
H11A	1.0843	0.8192	0.9127	5.0
H11B	1.1989	0.8284	0.8402	5.0
H11C	1.2552	0.7777	0.9388	5.0
H12	1.1697	0.6140	0.9453	4.4
H14	0.9264	0.7546	0.7162	6.1
H15	0.7754	0.6026	0.6342	7.5
H16	0.8072	0.4571	0.7081	5.9
H21A	0.6147	0.1498	0.8301	4.9
H21B	0.6005	0.0392	0.7919	4.9
H21C	0.7779	0.1116	0.8301	4.9
H22	0.5680	0.2668	0.7286	4.0
H24	0.6998	0.0251	0.6431	5.0
H25	0.6582	0.0795	0.4850	5.9
H26	0.5734	0.2267	0.4474	5.5
H31A	0.1069	0.0795	0.8200	5.0
H31B	0.3018	0.1342	0.8419	5.0
H31C	0.2302	0.0346	0.7763	5.0
H32	0.2041	0.0518	0.6179	4.2
H34	0.0838	0.2536	0.7747	5.1
H35	-0.0011	0.3358	0.6319	5.7
H36	0.0192	0.2779	0.4823	5.0
H41A	0.5952	0.7909	0.9501	4.0
H41B	0.5282	0.8277	0.8440	4.0
H41C	0.7110	0.8033	0.8800	4.0
H42	0.3793	0.7174	0.7110	4.3
H44	0.6709	0.6274	0.9616	5.5
H45	0.5640	0.4642	0.8949	6.3
H46	0.3655	0.4273	0.7384	6.0

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

Table SIV. Bond Angles (in degrees).

Cl(1)-Cu(1)-Cl(1)a	180.0		C(24)-C(25)-C(26)	121.3(5)
Cl(1)-Cu(1)-Cl(2)	89.46(5)		C(24)-C(25)-H(25)	119.3(5)
Cl(1)-Cu(1)-Cl(2)a	90.54(5)		C(26)-C(25)-H(25)	119.4(5)
Cl(1)-Cu(1)-Cl(3)	89.60(5)		C(21)-C(26)-C(25)	119.4(4)
Cl(1)-Cu(1)-Cl(3)a	90.40(5)		C(21)-C(26)-H(26)	119.8(5)
Cl(1)a-Cu(1)-Cl(2)	90.54(5)		C(25)-C(26)-H(26)	120.8(5)
Cl(1)a-Cu(1)-Cl(2)a	89.46(5)		C(33)-N(31)-H(31A)	105.1(3)
Cl(1)a-Cu(1)-Cl(3)	90.40(5)		C(33)-N(31)-H(31B)	107.5(3)
Cl(1)a-Cu(1)-Cl(3)a	89.60(5)		C(33)-N(31)-H(31C)	106.7(3)
Cl(2)-Cu(1)-Cl(2)a	180.0		H(31A)-N(31)-H(31B)	114.3(4)
Cl(2)-Cu(1)-Cl(3)	91.04(5)		H(31A)-N(31)-H(31C)	113.2(4)
Cl(2)-Cu(1)-Cl(3)a	88.96(5)		H(31B)-N(31)-H(31C)	109.5(4)
Cl(2)a-Cu(1)-Cl(3)	88.96(5)		Cl(31)-C(31)-C(32)	118.3(4)
Cl(2)a-Cu(1)-Cl(3)a	91.04(5)		Cl(31)-C(31)-C(36)	119.5(3)
Cl(3)-Cu(1)-Cl(3)a	180.0		C(32)-C(31)-C(36)	122.1(4)
H(21A)-Cl(5)-H(31B)	73.70(5)		C(31)-C(32)-C(33)	117.6(4)
C(13)-N(11)-H(11A)	105.5(3)		C(31)-C(32)-H(32)	121.1(4)
C(13)-N(11)-H(11B)	105.0(3)		C(33)-C(32)-H(32)	121.3(4)
C(13)-N(11)-H(11C)	105.5(3)		N(31)-C(33)-C(32)	118.5(4)
H(11A)-N(11)-H(11B)	114.8(4)		N(31)-C(33)-C(34)	119.6(4)
H(11A)-N(11)-H(11C)	115.5(4)		C(32)-C(33)-C(34)	122.0(4)
H(11B)-N(11)-H(11C)	109.5(4)		C(33)-C(34)-C(35)	118.7(4)
Cl(11)-C(11)-C(12)	118.9(4)		C(33)-C(34)-H(34)	120.7(5)
Cl(11)-C(11)-C(16)	119.0(4)		C(35)-C(34)-H(34)	120.6(5)
C(12)-C(11)-C(16)	122.1(4)		C(34)-C(35)-C(36)	120.7(4)
C(11)-C(12)-C(13)	117.6(4)		C(34)-C(35)-H(35)	119.3(5)
C(11)-C(12)-H(12)	121.2(4)		C(36)-C(35)-H(35)	120.0(5)
C(13)-C(12)-H(12)	121.2(4)		C(31)-C(36)-C(35)	118.8(4)
N(11)-C(13)-C(12)	119.2(4)		C(31)-C(36)-H(36)	120.6(5)
N(11)-C(13)-C(14)	118.8(4)		C(35)-C(36)-H(36)	120.6(5)
C(12)-C(13)-C(14)	122.0(4)		C(43)-N(41)-H(41A)	108.8(4)
C(13)-C(14)-C(15)	117.8(5)		C(43)-N(41)-H(41B)	109.0(3)
C(13)-C(14)-H(14)	121.3(5)		C(43)-N(41)-H(41C)	103.1(3)
C(15)-C(14)-H(14)	120.9(5)		H(41A)-N(41)-H(41B)	110.5(4)
C(14)-C(15)-C(16)	122.0(5)		H(41A)-N(41)-H(41C)	112.5(4)
C(14)-C(15)-H(15)	118.7(6)		H(41B)-N(41)-H(41C)	112.7(4)
C(16)-C(15)-H(15)	119.3(6)		Cl(41)-C(41)-C(42)	118.9(4)
C(11)-C(16)-C(15)	118.5(5)		Cl(41)-C(41)-C(46)	120.4(4)
C(11)-C(16)-H(16)	120.9(6)		C(42)-C(41)-C(46)	120.8(4)
C(15)-C(16)-H(16)	120.7(5)		C(41)-C(42)-C(43)	118.5(4)
C(23)-N(21)-H(21A)	104.2(3)		C(41)-C(42)-H(42)	120.7(4)
C(23)-N(21)-H(21B)	108.9(4)		C(43)-C(42)-H(42)	120.8(4)
C(23)-N(21)-H(21C)	108.5(3)		N(41)-C(43)-C(42)	118.9(4)
H(21A)-N(21)-H(21B)	113.0(4)		N(41)-C(43)-C(44)	119.2(4)
H(21A)-N(21)-H(21C)	112.3(4)		C(42)-C(43)-C(44)	121.8(4)
H(21B)-N(21)-H(21C)	109.6(4)		C(43)-C(44)-C(45)	118.3(5)
Cl(21)-C(21)-C(22)	119.3(4)		C(43)-C(44)-H(44)	120.8(5)
Cl(21)-C(21)-C(26)	120.2(3)		C(45)-C(44)-H(44)	120.9(5)
C(22)-C(21)-C(26)	120.5(4)		C(44)-C(45)-C(46)	121.0(5)
C(21)-C(22)-C(23)	118.5(4)		C(44)-C(45)-H(45)	119.2(5)
C(21)-C(22)-H(22)	120.5(4)		C(46)-C(45)-H(45)	119.9(5)
C(23)-C(22)-H(22)	120.9(4)		C(41)-C(46)-C(45)	119.6(4)
N(21)-C(23)-C(22)	119.3(4)		C(41)-C(46)-H(46)	120.2(5)
N(21)-C(23)-C(24)	118.8(4)		C(45)-C(46)-H(46)	120.2(5)
C(22)-C(23)-C(24)	121.9(4)		Cl(5)-H(21A)-N(21)	171.92(21)
C(23)-C(24)-C(25)	118.4(5)		Cl(5)-H(31B)-N(31)	170.36(21)
C(23)-C(24)-H(24)	120.8(5)		Cl(4)-H(41B)-N(41)	176.17(21)
C(25)-C(24)-H(24)	120.8(5)			

Table SV.   Bond Length (A).

Cu(1)-Cl(1)	2.2773(11)		C(24)-H(24)	0.960(5)
Cu(1)-Cl(1)a	2.2773(11)		C(25)-C(26)	1.370(8)
Cu(1)-Cl(2)	2.6061(18)		C(25)-H(25)	0.960(5)
Cu(1)-Cl(2)a	2.6061(18)		C(26)-H(26)	0.960(5)
Cu(1)-Cl(3)	2.6086(20)		Cl(31)-C(31)	1.741(5)
Cu(1)-Cl(3)a	2.6086(20)		N(31)-C(33)	1.475(5)
Cl(4)-H(41B)	2.2625(15)		N(31)-H(31A)	0.960(4)
Cl(5)-H(21A)	2.2605(14)		N(31)-H(31B)	0.960(4)
Cl(5)-H(31B)	2.2320(16)		N(31)-H(31C)	0.960(4)
Cl(11)-C(11)	1.734(5)		C(31)-C(32)	1.383(6)
N(11)-C(13)	1.473(6)		C(31)-C(36)	1.368(7)
N(11)-H(11A)	0.960(4)		C(32)-C(33)	1.371(6)
N(11)-H(11B)	0.960(4)		C(32)-H(32)	0.960(4)
N(11)-H(11C)	0.960(4)		C(33)-C(34)	1.378(7)
C(11)-C(12)	1.385(6)		C(34)-C(35)	1.382(7)
C(11)-C(16)	1.354(7)		C(34)-H(34)	0.960(5)
C(12)-C(13)	1.372(6)		C(35)-C(36)	1.377(7)
C(12)-H(12)	0.960(4)		C(35)-H(35)	0.960(5)
C(13)-C(14)	1.371(7)		C(36)-H(36)	0.960(4)
C(14)-C(15)	1.376(8)		Cl(41)-C(41)	1.730(5)
C(14)-H(14)	0.960(5)		N(41)-C(43)	1.471(5)
C(15)-C(16)	1.366(9)		N(41)-H(41A)	0.960(4)
C(15)-H(15)	0.960(5)		N(41)-H(41B)	0.960(4)
C(16)-H(16)	0.960(5)		N(41)-H(41C)	0.960(4)
Cl(21)-C(21)	1.730(5)		C(41)-C(42)	1.373(6)
N(21)-C(23)	1.477(5)		C(41)-C(46)	1.375(7)
N(21)-H(21A)	0.960(4)		C(42)-C(43)	1.381(6)
N(21)-H(21B)	0.960(4)		C(42)-H(42)	0.960(4)
N(21)-H(21C)	0.960(4)		C(43)-C(44)	1.368(7)
C(21)-C(22)	1.387(6)		C(44)-C(45)	1.383(7)
C(21)-C(26)	1.379(7)		C(44)-H(44)	0.960(5)
C(22)-C(23)	1.369(6)		C(45)-C(46)	1.369(8)
C(22)-H(22)	0.960(4)		C(45)-H(45)	0.960(5)
C(23)-C(24)	1.379(7)		C(46)-H(46)	0.960(5)
C(24)-C(25)	1.372(7)			

Table SVI. Torsion Angles.

CL11	C11	C12	C13	180.0(4)	C16	C11	C12	C13	0.3(2)
CL11	C11	C16	C15	-179.2(5)	C12	C11	C16	C15	0.5(3)
C11	C12	C13	N11	178.7(5)	C11	C12	C13	C14	0.1(3)
N11	C13	C14	C15	-179.8(5)	C12	C13	C14	C15	-1.2(3)
C13	C14	C15	C16	2.0(2)	C14	C15	C16	C11	-1.7(3)
CL21	C21	C22	C23	177.6(4)	C26	C21	C22	C23	-1.2(2)
CL21	C21	C26	C25	-177.6(5)	C22	C21	C26	C25	1.2(2)
C21	C22	C23	N21	-178.5(4)	C21	C22	C23	C24	0.6(2)
N21	C23	C24	C25	179.2(5)	C22	C23	C24	C25	0.1(2)
C23	C24	C25	C26	-0.1(2)	C24	C25	C26	C21	-0.5(2)
CL31	C31	C32	C33	178.7(4)	C36	C31	C32	C33	-0.1(2)
CL31	C31	C36	C35	-179.2(4)	C32	C31	C36	C35	-0.4(2)
C31	C32	C33	N31	179.6(4)	C31	C32	C33	C34	0.1(2)
N31	C33	C34	C35	-179.0(5)	C32	C33	C34	C35	0.4(2)
C33	C34	C35	C36	-0.9(2)	C34	C35	C36	C31	0.9(2)
CL41	C41	C42	C43	-179.6(4)	C46	C41	C42	C43	-0.3(2)
CL41	C41	C46	C45	179.8(5)	C42	C41	C46	C45	0.5(2)
C41	C42	C43	N41	-178.1(5)	C41	C42	C43	C44	-0.3(2)
N41	C43	C44	C45	178.4(5)	C42	C43	C44	C45	0.7(2)
C43	C44	C45	C46	-0.4(2)	C44	C45	C46	C41	-0.2(2)

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies		No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant . for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality		
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214
R&T Code 4135002

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907
R&T Code 4135011

Professor Steven L Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
R&T Code 4135014

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
R&T Code 4135007

Professor M. Frederick Hawthorne
Department of Chemistry
405 Hilgard Avenue
University of California
Los Angeles, CA 90024
R&T Code 4135004

Professor Robert H. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, TX 76843
R&T Code 4135005

Professor Kurt Niedenzu
Department of Chemistry
University of Kentucky
Lexington, KY 40506
R&T Code 4135003

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706
R&T Code 4135008